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VI.

A METHOD FOR THE SEPARATION OF SODIUM AND
POTASSIUM FROM LITHIUM BY THE ACTION
OF AMYL ALCOHOL ON THE CHLORIDES,WITH SOME REFERENCE TO A SIMILAR SEPARATION OF
THE SAME FROM MAGNESIUM AND CALCIUM.

BY F. A. GOOCH.

Presented June 16, 1886.

For the quantitative separation of lithium from sodium and potassium, Mayer's method,* which is based upon the precipitation of lithium as the tribasic phosphate, and Rammelsberg's † mode of parting the chlorides by means of a mixture of anhydrous alcohol and ether in equal parts have been available.

The method of Mayer grew out of the older process of Berzelius,‡ which consisted essentially in treating the solution of the alkaline salts with phosphoric acid and sodium carbonate in excess, evaporating to dryness, and extracting with cold water. The result of a single analysis of the product thus obtained was the testimony upon which Berzelius rested the belief and statement that the salt was a double phosphate of lithium and sodium, which left upon ignition sodium and lithium pyrophosphates in equal molecules; and on this Berzelius based his process for the estimation of lithium. Rammelsberg,§ however, showed later that it was a tribasic phosphate which was actually obtained, and from his experiments arrived at the conclusion that the proportion of soda and lithia were variable within wide limits, the amounts of the former varying in the special cases investigated from 7.84% to 28.38%; and the same thing in substance was reiterated subsequently || in an account of a repetition of the work suggested by the criticism of Mayer. Mayer,¶ however, was unable to prepare under any conditions the double phosphate of Rammelsberg, and obtained invariably, when the preparation had been washed with suffi-

* Ann. d. Chem. u. Pharm., xcvi. 193.

§ Loc. cit.

† Pogg. Ann., lxvi. 79.

|| Pogg. Ann., cii. 443.

‡ Ibid., iv. 245.

¶ Loc. cit.

cient care, trillithium phosphate free from sodium; but the point was made, that the phosphate is apt to be contaminated with lithium carbonate when sodium carbonate is employed to bring about alkalinity. Mayer therefore modifies the method of Berzelius by substituting sodium hydrate for the carbonate; and, proceeding, evaporates to dryness, treats the dry mass with as much water as is needed to dissolve the soluble salts with the aid of heat, adds a drop or two of sodium hydrate if necessary to restore alkalinity and then ammonia in volume equal to that of the water already added, sets aside at a gentle heat, filters only after twelve hours, and washes with a mixture of ammonia and water in equal parts. From the filtrate and first washings a small amount of the lithium phosphate is to be recovered by evaporation and the repetition of the former treatment. According to Mayer, the precipitation of the phosphate may be effected with equal completeness by boiling the solution, prepared as before, instead of evaporating it; but the objection to this mode of proceeding is the tendency of the liquid carrying the precipitate to bump explosively. Careful washing, somewhat prolonged, is essential to secure the complete removal of salts of sodium and potassium, and it is remarked that the purity of the precipitate is shown by its failure to cake when strongly ignited.

This is the mode of proceeding by which Mayer separates lithium from sodium and potassium, isolating it as presumably pure tri-lithium phosphate and weighing it as the anhydrous salt. In dealing with mixtures of the chlorides in which the proportion of the lithium salt is relatively small, the removal of the greater part of sodium and potassium chlorides by a preliminary treatment with absolute alcohol is recommended. The following table comprises the results of Mayer's test analyses of lithium carbonate in the first seven, of lithium sulphate in the last two, recalculated with the use of the number 7 — the figure now generally accepted — as the atomic weight of lithium.

Li_3PO_4 equivalent to Salt taken.	Li_3PO_4 found.	Error.
1.3586 grm.	1.3719 grm.	0.0133+ grm.
1.5172 "	1.5088 "	0.0084— "
0.7519 "	0.7580 "	0.0061+ "
0.9561 "	0.9510 "	0.0051— "
1.2651 "	1.2646 "	0.0005— "
1.2197 "	1.2230 "	0.0033+ "
0.8991 "	0.9018 "	0.0027+ "
1.1325 "	1.1236 "	0.0089— "
0.9715 "	0.9665 "	0.0050— "

Fresenius* found on examining the method that several repetitions of the treatment by evaporation and extraction were required to complete the recovery of all lithium phosphate, and advised that the operation be continued until residual lithium phosphate fails to appear. The results of Fresenius's experiments with lithium carbonate, recalculated with the use of the number 7 as the atomic weight of lithium, are given in the table appended.

Li ₃ PO ₄ equivalent to Salt taken.		Li ₃ PO ₄ found.		Error.
gram.		Dried at 100° C. gram.	Ignited. gram.	gram.
0.7443	{ after two treatments	0.7243	0.0200—
	{ " three "	0.7385	0.0058—
	{ " four "	0.7433	0.0010—
0.9820	{	0.9861	0.0041+
		0.9826	0.0006+
1.6341	{	1.6342	0.0001+
		1.6305	0.0036—

Thus it will be seen that in the nine experiments of Mayer the error ranges from 0.0133+ gram. to 0.0089— gram., and that of the determinations of Fresenius from 0.0001+ gram. to 0.0041+ gram. for the dried precipitate, and from 0.0006+ gram. to 0.0036— gram. for the ignited precipitate.

If the tendency of lithium carbonate to fall in company with the phosphate were not to assert itself during the evaporations of solutions of salts of lithium in presence of sodium hydrate and in contact with ordinary atmospheric air, it would surely be strange, and this point may be fairly set down as one of the weak ones of the method; but the gravest source of error, and that indicated most unmistakably throughout the whole history of the process,—which has been recounted at some length for the purpose of emphasizing this very matter,—is the impossibility of preparing the lithium phosphate in anything like a condition of freedom from other alkaline phosphates without a careful and prolonged washing which is sure to result in loss of the lithium salt by solution. When it is remembered that according to Mayer's determinations tri-lithium phosphate requires for solution only 2539 parts of water, or 3920 parts of a mixture of ammonia and water in equal portions, it is plain that the success of the method depends upon the ability of the analyst to wash to a condition of purity, and without loss of that which it is the purpose of the

process to save, a precipitate peculiarly prone to retain foreign matter and soluble in the washing mixture in the proportion of ten milligrams to every 40 cm.³ of the latter. Of course washings will never be entirely saturated, nor will the precipitate be as soluble at the beginning of the operation as at the end, when the precipitant no longer exerts an action which tends to lessen solubility; but in view of the difficulties which present themselves, it is sufficiently obvious that exact results obtained by Mayer's process owe their apparent accuracy to a fortuitous balance of errors. The difference of 0.0222 grm. between the extremes of Mayer's experimental results should not be surprising; and, at the best, the process is tedious and not entirely trustworthy, — facts of which its author was not unmindful.

In Rammelsberg's method of separating lithium chloride from the chlorides of sodium and potassium the sources of error are, in brief, the solubility of sodium chloride and potassium chloride in the ether-alcohol mixture, the influence which the presence of small amounts of water exerts upon the solubility of these same salts, the difficulty of bringing the chlorides to the anhydrous condition without decomposing the lithium chloride to a greater or less extent, and the mechanical difficulties of transferring the fused or crusted chlorides to a suitable receptacle for digestion and agitation in the solvent, and of extracting perfectly the soluble constituents of closely compacted matter. Of the last two items nothing need be said in explanation beyond simply noting them. The third is particularly important, inasmuch as the tendency of lithium chloride, first noted I believe by Mayer, to exchange chlorine for oxygen when ignited in presence of water, results in the formation of lithium hydrate or, in contact with products of combustion, lithium carbonate, both of which are insoluble in the mixture of ether and alcohol, and remain with the sodium and potassium chlorides. As to the effect of water in the mixture, an experiment of Mayer, in which it was found that 100 cm.³ of a mixture of alcohol of 96% and ether of 98% dissolved 0.1100 grm. of sodium chloride, is instructive. In regard to the solubility of the chlorides of sodium and potassium in the mixture of anhydrous ether and alcohol, Rammelsberg's statement, that from 0.9770 grm. of pure strongly heated sodium chloride with an undetermined amount of lithium chloride the mixture extracted 0.0130 grm., is unfortunately meaningless in the absence of information concerning the amount of solvent employed. J. Lawrence Smith* found, in making an exami-

* Am. Jour. Sci. [2], xvi. 56.

nation of this matter, that 10 cm.³ of the anhydrous ether-alcohol mixture extracted from 0.5 grm. of sodium chloride 0.0005 grm., and from 0.5 grm. of potassium chloride 0.0003 grm. Smith's mode of applying the method is better than the original; for, by taking care not to heat the mixed salts above 100° C., the danger of decomposing the lithium chloride is diminished, and by treating the dried salts with the ether-alcohol mixture in the capsule in which it is heated and weighed (protecting it by a small inverted bell-glass) the disadvantage of the transfer is avoided, but the danger is incurred that the mixed salts may not be thoroughly dried by heat so gentle. With this modification Smith obtained results which are rearranged in the following statement, and which do not throw a very favorable light upon the method.*

NaCl taken. grm.	KCl taken. grm.	LiCl taken. grm.	Weight dissolved. grm.	Error. grm.
0.2000	0.2000	0.0080	0.0101	0.0021+
0.2000	0.2000	0.0884	0.0862	0.0022—
0.2000	0.2000	0.8195	0.8341	0.0146+

It is obvious, therefore, that neither the method of Rammelsberg nor that of Mayer may justly claim to be what a good process should be, accurate and rapid; and in the dilemma many chemists have been inclined to accept, with Bunsen,† the inherent disadvantage of an indirect process, and in a mixture of sodium and lithium chlorides calculate the percentage of each from the known weight of the mixture and its contents in chlorine, and in a mixture of the three chlorides calculate the percentage of each from the known weight of the mixture and the determined contents in chlorine and potassium. Here again, however, as in Rammelsberg's process, the difficulty of bringing the chlorides to a definite condition for weighing without decomposing

* Dr. Smith's language in the description of these experiments is somewhat ambiguous, but it is believed that these figures represent the meaning intended. After the presentation of the data of the first experiment given here with the correction of an obvious typographical error, it is said of the second and third experiments that "a similar mixture containing 18.10 per cent of chloride of lithium furnished a residue of 17.65 per cent," and "a similar mixture containing 67.20 per cent of chloride of lithium gave a residue of 68.40." I have taken this to mean that in all three experiments 0.2 grm. of sodium chloride and 0.2 grm. of potassium chloride were employed with the different proportions of lithium chloride indicated for each experiment. At all events, if this is not the meaning of the language made use of, it is difficult to see a definite value in the experiments.

† Ann. d. Chem. u. Pharm., cxxii. 348.

the lithium chloride is an obstacle; and in case potassium is to be separated from large amounts of lithium by precipitation as potassio-platinic chloride, the concurrent precipitation of a similar salt of lithium, to which Jenzsch * has directed attention, may be the occasion of inexactness. So, the intrinsic unsatisfactoriness of indirect methods quite aside, it appears that in following Bunsen we have by no means all that is to be desired in an analytical method.

In looking about for better means for the separation of lithium from sodium and potassium, certain preliminary experiments on the behavior of the chlorides of these elements toward amyl alcohol gave very encouraging indications, and subsequent quantitative tests have borne out the hope that a successful method of separation might be based upon these relations.

In amyl alcohol the chlorides of sodium and potassium are highly insoluble, lithium chloride dissolves freely, and the attraction of amyl alcohol for water is so slight and its boiling point so far above 100°C . that the latter may be expelled without difficulty by the aid of gentle heating.

When amyl alcohol is poured into a solution of lithium chloride in water the liquid forms two layers, the aqueous solution of the salts at the bottom and the amyl alcohol now carrying a little water above. With the application of heat, the water evaporates slowly, then boils, and, passing through the alcohol, escapes, until toward the end of the operation the residual lithium chloride collects in a viscous globule, and finally dissolves with the exception of a slight incrustation. If now the alcohol is cooled and a drop of strong hydrochloric acid added and brought in contact with the deposit, and the boiling repeated, the solution is complete. This deposit I take to be lithium hydrate, resulting from the decomposition of the chloride by the protracted action of water at a temperature near its boiling point. The small amount of water which is added in and with the hydrochloric acid seems to exert no unfavorable influence, but rather to be beneficial in hastening the solution of the residue by securing immediate and sufficient contact.

In hot amyl alcohol, lithium chloride appears to be a little more soluble than in the same reagent at ordinary temperatures, but the solubility under the latter condition only was determined. By boiling the solution until turbidity began to show, cooling, filtering, and then evaporating a known volume of the concentrated solution to dryness

* Pogg. Ann., civ. 102.

and weighing the residue after converting it to the sulphate, it was found that one part of lithium chloride was held dissolved in the cold in about fifteen parts of amyl alcohol, 10 cm.³ of the solution containing in the mean 0.66 grm. of the chloride.

When aqueous solutions of sodium chloride or potassium chloride are treated with amyl alcohol and boiled, the water disappears, as before, leaving first a globule of the concentrated solution and finally the crystalline salts. On continuing the boiling until a thermometer dipped in the liquid indicates the temperature at which the alcohol boils by itself, a slight additional precipitation, doubtless due to the expulsion of the water retained by the alcohol up to this point, takes place upon the walls of the containing vessel. The results of quantitative tests of the solubility of sodium and potassium chlorides are given in the following tables. The strength of the solutions of sodium chloride and potassium chloride were determined by evaporating weighed portions in a platinum crucible and drying at a temperature considerably below the melting point of the salt, and weighing. The solution of lithium chloride was standardized by treating a weighed portion with sulphuric acid in excess, evaporating, igniting at red heat, and weighing. The standards were fixed by experiments (1) to (9).

Weight of Solution of NaCl taken. grm.	Weight of NaCl found. grm.	Weight of NaCl in 10 grm. of Solution. grm.	Mean.
(1) 10.7110	0.1072	0.1001	} grm. 0.1002
(2) 10.9419	0.1097	0.1003	
(3) 10.9325	0.1097	0.1003	

Weight of Solution of KCl taken. grm.	Weight of KCl found. grm.	Weight of KCl in 10 grm. of Solution grm.	Mean.
(4) 9.3045	0.1744	0.1874	} grm. 0.1872
(5) 10.7225	0.2006	0.1871	
(6) 11.1974	0.2096	0.1872	

Weight of Solution of LiCl taken. grm.	Weight of Li ₂ SO ₄ found. grm.	Weight of LiCl in 10 grm. of Solution. grm.	Mean.
(7) 10.9280	0.1635	0.1156	} grm. 0.1154
(8) 11.1480	0.1665	0.1153	
(9) 10.8790	0.1626	0.1154	

To determine the solubility of sodium chloride and potassium chloride in amyl alcohol, portions of the test solutions were weighed out,

evaporated to a convenient bulk in platinum crucibles of 100 cm.³ capacity, amyl alcohol was added, the water expelled by boiling, and the heating continued for some minutes after the thermometer in the liquid indicated 132° C., the boiling point of the alcohol employed. The liquid was then decanted with care and the residue dried at a temperature below its melting point and weighed. When the chlorides are precipitated in the manner described, the deposit generally adheres so closely, and such particles as do remain loose settle so well, that the supernatant liquid may be decanted to the end without appreciable transportation of the insoluble residue. For the sake of perfect security, however, in this part of the manipulation the decanted liquid was filtered under gentle pressure upon asbestos, with the aid of the device which I have previously described for such purposes,* and, after gentle heating, the increase in weight of the felt and the containing perforated crucible added to the weight of the residual salt. In no case did this increase exceed a few tenths of a milligram, and often could not be detected.

As a source of heat, a bath in which the sand of the sand-bath is replaced by smooth asbestos board is a convenience, or a piece of asbestos board simply, about 30 cm. square, supported by a broad tripod and heated under the middle by a Bunsen burner, answers equally well to secure every gradation of heat without danger of igniting the evaporated alcohol.

As a control upon the results obtained by weighing the residue as described, the filtrate was evaporated in a large platinum crucible, and the residue thus left gently heated and weighed. Though the evaporation be conducted with extreme care, the residue is almost sure to show some blackening, due to the carbonization of matter carried by the alcohol, which will not disappear entirely without the application of a degree of heat which the salts cannot bear without danger of volatilization. The weight of the residue from the amyl alcohol itself is small, — one portion of 50 cm.³ yielding 0.0003 gm. and its mate 0.0007 gm., — so that the data obtained by the evaporation of the filtered alcohol of the experiments, if not quite so trustworthy as the former testimony, may nevertheless serve the purpose of a very close control. Both sets of data are given in the following table.

* These Proceedings, Vol. XIII. p. 342.

	Weight of NaCl taken.	Total Weight of NaCl found.	Weight found in Residue.	Weight found in Solution.	Volume of re- sidual Amyl Alcohol.
	gram.	gram.	gram.	gram.	cm. ³
{ (10)	0.1062	0.1067	0.1043	0.0024	52
{ (11)	0.1043	0.1047	0.1024	0.0023	46
{ (12)	0.1024	0.1030	0.1003	0.0027	51
{ (13)	0.1003	0.1008	0.0983	0.0025	45

Reducing these figures to a common level to show the action of the same amount of amyl alcohol in every case we have:—

	Loss of NaCl to 100 cm. ³ of Amyl Alcohol.	Mean.	Weight of NaCl found in Solution in 100 cm. ³ of Amyl Alcohol.	Mean.
	gram.		gram.	
{ (10)	0.0037	gram. 0.0041	0.0046	gram. 0.0051
{ (11)	0.0041		0.0050	
{ (12)	0.0041		0.0053	
{ (13)	0.0044		0.0055	

	Weight of KCl taken.	Total Weight of KCl found.	Weight found in Residue.	Weight found in Solution.	Volume of re- sidual Amyl Alcohol.
	gram.	gram.	gram.	gram.	cm. ³
{ (14)	0.2091	0.2093	0.2074	0.0019	35
{ (15)	0.2074	0.2078	0.2059	0.0019	36
{ (16)	0.2059	0.2059	0.2040	0.0019	32
{ (17)	0.2040	0.2041	0.2015	0.0026	45

Derived from these figures we have:—

	Loss of KCl to 100 cm. ³ of Amyl Alcohol.	Mean.	Weight of KCl found in Solution in 100 cm. ³ of Amyl Alcohol.	Mean.
	gram.		gram.	
{ (14)	0.0049	gram. 0.0051	0.0054	gram. 0.0056
{ (15)	0.0041		0.0053	
{ (16)	0.0059		0.0059	
{ (17)	0.0056		0.0058	

From these figures it appears that the total weight of chloride found is always a little greater than that taken, the mean increase being 0.0005 gram. for sodium chloride, and 0.0002 gram. for potassium chloride. It appears also that the residue left by the evaporation of the decanted and filtered amyl alcohol is greater than the loss put upon the chloride by the treatment,—in the case of sodium chloride 0.0005 gram., in the mean, for every 50 cm.³ of amyl alcohol, which is about the quantity employed in the experiments; for potassic chlo-

ride 0.0002 grm., in the mean, for 40 cm.³ of amyl alcohol, which is approximately the quantity used in that case. It will be seen, therefore, that there exists for both salts an exact coincidence between the mean total excess found and the difference between the figures which indicate the solubility of the salts for the two methods of determination; and, taking this fact in conjunction with the results of the evaporation of amyl alcohol in blank, — the mean residue being 0.0004 grm. for 40 cm.³, and 0.0005 grm. for 50 cm.³, — it seems to be brought out pretty clearly that the former set of figures represents more exactly the solubility of the salts, though the difference between the two series is not great. Resting, then, upon the former determinations, the solubility of sodium chloride may be taken as 0.0041 grm. in every 100 cm.³ of anhydrous amyl alcohol, or one part in 30,000 parts by weight; and the solubility of potassium chloride, a little greater, is 0.0051 grm. to 100 cm.³ of amyl alcohol, or one part in 24,000 by weight.

The conditions under which the salts are acted upon are such as should insure the complete saturation of the solvent, and in this connection it is interesting to note that for the quantities of material employed the discrepancy between comparable figures never exceeds 0.0005 grm.

In experiments (10), (11), and (14), (15), the alcohol was decanted and filtered at once while hot; in (12), (13), and (16), (17), it was cooled to 30° C. before decanting; so it appears that the solubility of the salts is not influenced by changes of temperature within the range from 30° C. to 132° C.

Used simply to wash the precipitate, amyl alcohol cannot, of course, exert an effect at all comparable with that manifested in the experiments which have been described, but to know just what this action may be is important. Experiments (18) to (22) were undertaken, therefore, to elucidate this point.

Weighed amounts of the test solutions were evaporated nearly to saturation in small glass beakers, amyl alcohol added, and, as in the previous experiments, the whole heated until the salt had deposited and the residual alcohol had boiled quietly for some minutes at its ordinary boiling point, the liquid decanted, filtered under gentle pressure by means of a weighed perforated crucible and felt of asbestos, the filtrate measured, the residue dislodged with the aid of a rubbing-rod and transferred to the crucible and washed with anhydrous amyl alcohol, the washings being collected and measured. The crucible and contents were dried over a free flame turned low so that the heat should not reach the melting point of the chlorides.

	Weight of NaCl taken.	Weight of NaCl found.	Weight of NaCl found, corrected for Solubility in resid- ual Amyl Alcohol.	Error of cor- rected Weight of NaCl found.	Volume of residual Amyl Alcohol.	Volume of Amyl Alco- hol in Washings.
	grm.	grm.	grm.	grm.	cm. ³	cm. ³
(18)	0.0947	0.0937	0.0947	0.0000	24	44
(19)	0.1080	0.1074	0.1082	0.0002+	19	53

	Weight of KCl taken.	Weight of KCl found.	Weight of KCl found, corrected for Solubility in resid- ual Amyl Alcohol.	Error of cor- rected Weight of KCl found.	Volume of residual Amyl Alcohol.	Volume of Amyl Alco- hol in Washings.
	grm.	grm.	grm.	grm.	cm. ³	cm. ³
(20)	0.1846	0.1837	0.1847	0.0001+	20	60
(21)	0.1964	0.1946	0.1961	0.0003—	30	45
(22)	0.1857	0.1839	0.1854	0.0003—	30	60

These results show very plainly that the solvent effect of anhydrous amyl alcohol used for washing under the conditions described is trifling in the extreme, and may be neglected utterly providing the amount of the washing is not altogether disproportionate to the needs of the case.

We pass next to the consideration of the separation of the chlorides of sodium and potassium from lithium chloride. Weighed portions of the test solutions were concentrated and treated with amyl alcohol in the manner described until the precipitated salt was entirely free from water and the supernatant alcoholic solution of the lithium chloride boiled constantly at a point not far from that of the amyl alcohol employed. Then the liquid was cooled, a drop or two of strong hydrochloric acid added in accordance with the evident suggestion of the preliminary experiments previously mentioned, and heat again applied until the boiling had continued, as before, for some minutes at one point. The filtration, washing, drying, and weighing of the residue were effected as in experiments (18) to (22). In those of the experiments in which the lithium salt in solution was also determined, the end was accomplished by evaporating the filtrate and washings to dryness, treating the residue with sulphuric acid, and igniting and weighing as lithium sulphate. In the following table the weight of insoluble chloride actually found is given in one column, and this weight, corrected according to the data previously determined for the solubility of the chloride in the residual amyl alcohol appears in the column adjoining. So also the weight is given of the lithium sulphate actually found, and an adjacent column contains the result of correcting this weight for the accompanying sodium or potassium sulphate, or both, upon the hypothesis that these salts are neutral sulphates

after the ignition. In the case of quantities so minute the error which is introduced by such an assumption cannot be considerable, and in relation to this point Dittmar* maintains that comparatively large amounts of acid sodium or potassium sulphate may be reduced to the neutral salt by ignition simply. The figures of the column showing the weights of lithium chloride found are derived by calculation from the weights of lithium sulphate actually found. The other headings of the table are sufficiently intelligible without further explanation.

	Weight of NaCl taken.	Weight of NaCl found.	Weight of NaCl found, corrected for Solubility in Amyl Alcohol.	Error in Weight of NaCl found.	Error in corrected Weight of NaCl found.	Volume of Amyl Alcohol used.	
	gram.	gram.	gram.	gram.	gram.	Resid- ual. cm. ³	Total. cm. ³
(23)	0.1089	0.1092	0.1095	0.0003+	0.0006+	7	70
(24)	0.1084	0.1085	0.1090	0.0001+	0.0006+	12	80
(25)	0.1074	0.1067	0.1074	0.0007—	0.0000	18	90

	Weight of LiCl taken.	Weight of Li ₂ SO ₄ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in corrected Weight of LiCl found.
	gram.	gram.	gram.	gram.	gram.	gram.
(23)	0.1298	0.1682	0.1299	0.1296	0.0001+	0.0002—
(24)	0.1227	0.1592	0.1230	0.1225	0.0003+	0.0002—
(25)	0.0116

	Weight of KCl taken.	Weight of KCl found.	Weight of KCl found, corrected for Solubility in Amyl Alcohol.	Error in Weight of KCl found.	Error in corrected Weight of KCl found.	Volume of Amyl Alcohol used.	
	gram.	gram.	gram.	gram.	gram.	Resid- ual. cm. ³	Total. cm. ³
(26)	0.2051	0.2036	0.2053	0.0015—	0.0002+	34	100
(27)	0.2022	0.2013	0.2032	0.0009—	0.0010+	37	100
(28)	0.2109	0.2096	0.2104	0.0013—	0.0005—	16	100
(29)	0.0984	0.0970	0.0980	0.0014—	0.0004—	20	90

	Weight of LiCl taken.	Weight of Li ₂ SO ₄ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in corrected Weight of LiCl found.
	gram.	gram.	gram.	gram.	gram.	gram.
(26)	0.1256	0.1638	0.1265	0.1248	0.0009+	0.0008—
(27)	0.1287	0.1677	0.1296	0.1277	0.0009+	0.0010—
(28)	0.0113
(29)	0.0113

* Report on Researches into the Composition of Ocean Water, collected by H. M. S. Challenger during the Years 1873-1876, p. 18.

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl + KCl found.	Corrected Weight of NaCl + KCl found.	Volume of Amyl Alcohol used.	
	gram.	gram.	gram.	gram.	Residual. cm. ³	Total. cm. ³
(30)	0.1053	0.1031	0.2064	0.2084	22	100
(31)	0.1051	0.0945	0.1988	0.2003	16	80

	Weight of LiCl taken.	Error in Weight of NaCl + KCl found.	Error in corrected Weight of NaCl + KCl found.
	gram.	gram.	gram.
(30)	0.0113	0.0020—	0.0000
(31)	0.0113	0.0008—	0.0007+

It will be noticed that in experiments (23), (24), (26), and (27), the corrected error in the weight of the insoluble chloride has a positive value ranging from $0.0002 +$ gram. to $0.0010 +$ gram. with a mean of $0.0006 +$ gram.; and that in experiments (25), (28), (29), (30), and (31), the mean error is negative, amounting to less than $0.0001 -$ gram., with a range from $0.0005 -$ gram. to $0.0007 +$ gram.

The point of difference between these two series of experiments is the amount of lithium chloride introduced, only a tenth of that used in the former being employed in the latter. It is plain that, when we are dealing with the larger amount, a larger portion tends to remain behind with the insoluble chloride; and here again we meet, though to a degree comparatively harmless, the inclination of lithium chloride to yield chlorine and pass to the form of lithium hydrate. When the lithium chloride is present in small amount, as in the latter group of experiments, there can be little left undissolved; and the spectroscope confirms the evidence of the figures of analysis as to the perfectness of the separation, by showing in such cases either no lithium at all or merely fugitive traces. If a single precipitation is sufficient to effect a satisfactory separation of the insoluble chlorides from small amounts of lithium chloride, it is natural to suppose that a repetition of the precipitation would be beneficial in treating larger quantities of lithium chloride. Experiments (32) to (37) illustrate the effect of a double precipitation. The chlorides were brought to filtration as before, the liquid was decanted as completely as possible, the precipitate washed slightly by decantation and redissolved in a little water, and the round of boiling, filtering, drying, and weighing carried to the end as before, care being taken to repeat the treatment with a drop of hydrochloric acid during the process of boiling. The two portions of residual amyl alcohol were measured apart, as well as the washings.

	Weight of NaCl taken.	Weight of NaCl found.	Corrected Weight of NaCl found.	Error in Weight of NaCl found.	Error in corrected Weight of NaCl found.	Volume of Amyl Alcohol used. Residual. Total.		
	gram.	gram.	gram.	gram.	gram.	I. II.	cm. ³ cm. ³	cm. ³
(32)	0.1166	0.1163	0.1169	0.0003—	0.0003+	8 8	150	
(33)	0.1139	0.1127	0.1132	0.0012—	0.0007—	5 7	150	

	Weight of LiCl taken.	Weight of Li ₂ SO ₄ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in corrected Weight of LiCl found.
	gram.	gram.	gram.	gram.	gram.	gram.
(32)	0.1287	0.1662	0.1284	0.1280	0.0003—	0.0007—
(33)	0.1347	0.1759	0.1359	0.1353	0.0012+	0.0006+

	Weight of KCl taken.	Weight of KCl found.	Corrected Weight of KCl found.	Error in Weight of KCl found.	Error in corrected Weight of KCl found.	Volume of Amyl Alcohol used. Residual. Total.		
	gram.	gram.	gram.	gram.	gram.	I. II.	cm. ³ cm. ³	cm. ³
(34)	0.1155	0.1142	0.1152	0.0013—	0.0003—	10 10	100	
(35)	0.1034	0.1017	0.1028	0.0017—	0.0007—	10 12	200	
(36)	0.1914	0.1905	0.1912	0.0009—	0.0002—	3 11	90	
(37)	0.1953	0.1939	0.1950	0.0014—	0.0003—	4 18	110	

	Weight of LiCl taken.	Weight of Li ₂ SO ₄ found.	Weight of LiCl found.	Corrected Weight of LiCl found.	Error in Weight of LiCl found.	Error in corrected Weight of LiCl found.
	gram.	gram.	gram.	gram.	gram.	gram.
(34)	0.1125	0.1475	0.1139	0.1128	0.0014+	0.0003+
(35)	0.1251	0.1649	0.1274	0.1162	0.0023+	0.0011+
(36)	0.1263
(37)	0.1282

Thus it appears that, in the separation of the insoluble chlorides from the larger amounts of lithium chloride, the residue of two precipitations is substantially free from lithium.

For the sake of bringing the data in hand more directly into comparison, the corrected errors of the preceding determinations are tabulated again in the following statement.

No. Exp.	Chloride.	CORRECTED ERROR OF INSOLUBLE CHLORIDE			Error in corrected Weight of LiCl.	Approximate Mean Error of LiCl.
		precipitated once from about 0.13 gm. of LiCl.	precipitated once from about 0.013 gm. of LiCl.	precipitated twice from about 0.13 gm. of LiCl.		
		gm.	gm.	gm.	gm.	
(23)	NaCl	0.0006+	0.0002—	} 0.0005— gm.
(24)	"	0.0006+	0.0002—	
(26)	KCl	0.0002+	0.0008—	
(27)	"	0.0010+	0.0010—	
(25)	NaCl	0.0000	
(28)	KCl	0.0005—	
(29)	"	0.0004—	
(30)	NaCl+KCl	0.0000	
(31)	" "	0.0007+	
(32)	NaCl	0.0003+	0.0007—	} 0.0003+ gm.
(33)	"	0.0007—	0.0006+	
(34)	KCl	0.0003—	0.0003+	
(35)	"	0.0007—	0.0011+	
(36)	"	0.0002—	
(37)	"	0.0003—	
Approx. mean,		0.0006+	0.00004—	0.0003—		

Few processes in analytical chemistry are capable of yielding results more exact than these. The separation of from 0.1 gm. to 0.2 gm. of sodium or potassium chloride from a tenth of its own weight of lithium chloride is practically perfect in one operation, and from its own weight of lithium chloride the parting may be effected satisfactorily by two precipitations.

The points to be observed in executing the method may be recapitulated as follows:—

To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until, the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a temperature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small it will now be found in solution, and the chlorides of sodium and potassium will be in the residue,

excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds ten or twenty milligrams, it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol previously dehydrated by boiling is to be used, and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0.00041 grm. for every 10 cm.³ of amyl alcohol in the filtrate exclusive of washings if the insoluble salt is entirely sodium chloride, 0.00051 grm. for every 10 cm.³ if potassium chloride constitutes the residue, and if both sodium and potassium chloride are present, 0.00092 grm.; but, as in the experiments described, the entire correction may in any case be kept within narrow limits, if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0.00050 grm. is to be made if sodium chloride constitutes the precipitate, 0.00059 grm. if potassium chloride alone is present in the residue, and 0.00109 if both of these chlorides are present, for every 10 cm.³ of filtrate exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as myself, for the estimation of lithium in waters and minerals.

In this connection it seems best to include the record of certain experiments looking to the separation of the chlorides of sodium and potassium from the chlorides of magnesium and calcium. The behavior of magnesium chloride toward amyl alcohol is of interest, both with reference to the problem of separating sodium and potassium from lithium and magnesium when the latter are associated, and as

concerns the parting of the alkalis from magnesium alone, — a matter which is by no means perfectly simple, — and experiments (38) to (41) touch upon this topic.

The chlorides of sodium and potassium were weighed, as before, in solution; the magnesium chloride was obtained by dissolving in hydrochloric acid the oxide specially prepared and weighed as such. The process of treatment was identical with that just described for the separation of the chlorides of potassium and sodium from lithium chloride.

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl + KCl found.	Corrected Weight of NaCl + KCl found.	Volume of Amyl Alcohol used.		Total.
					Residual.		
	gram.	gram.	gram.	gram.	I. cm. ³	II. cm. ³	cm. ³
(38)	0.1030	0.1064	0.2079	0.2100	23	..	120
(39)	0.0967	0.1024	0.1976	0.2006	33	..	100
(40)	0.1030	0.1073	0.2071	0.2093	13	11	100
(41)	0.1053	0.1093	0.2114	0.2142	12	18	100

	Weight of MgO taken.	Error in Weight of NaCl + KCl found.	Error in corrected Weight of NaCl + KCl found.
	gram.	gram.	gram.
(38)	0.1000	0.0015—	0.0006+
(39)	0.1000	0.0015—	0.0015+
(40)	0.1000	0.0032—	0.0010—
(41)	0.1000	0.0032—	0.0004—

The residues of experiments (38) and (39), in which the separation was made by a single precipitation, carried traces of magnesia; those of (40) and (41), in which two precipitations were introduced, were found to contain in the one case no magnesia, and in the other an unweighable trace. These results point out a method by which the chlorides of sodium and potassium may be obtained free from magnesia, while the small amounts of the former which pass into solution with the magnesium chloride are capable of accurate estimation; and there seems to be no reason why the separation of these alkaline chlorides from magnesium chloride and lithium chloride occurring together should not be effected in one operation, and the parting of the latter salts brought about by the familiar method of precipitating the magnesia in the cold as ammonium-magnesium phosphate.

Experiments (42) to (48), upon the separation of sodium and potassium from calcium by the action of amyl alcohol on the chlorides, yielded the figures of the following table. The mode of treatment was identical with that of the experiments with magnesia, just de-

scribed, excepting only the substitution of pure calcium oxide, specially prepared, for magnesium oxide.

	Weight of NaCl taken.	Weight of KCl taken.	Weight of NaCl + KCl found.	Corrected Weight of NaCl + KCl found.	Volume of Amyl Alcohol used.		Total.
	gram.	gram.	gram.	gram.	I. cm. ³	II. cm. ³	
(42)	0.0859	0.1126	0.2177	0.2195	20	..	100
(43)	0.1018	0.1057	0.2217	0.2235	20	..	100
(44)	0.1096	0.0962	0.2112	0.2130	20	..	100
(45)	0.0985	0.1018	0.2113	0.2130	19	..	100
(46)	0.0914	0.1104	0.1968	0.2000	20	15	100
(47)	0.0997	0.1100	0.2080	0.2089	3	7	90

	Weight of CaO taken.	Error in Weight of NaCl + KCl found.	Error in corrected Weight of NaCl + KCl found
	gram.	gram.	gram.
(42)	0.1000	0.0192+	0.0210+
(43)	0.1000	0.0142+	0.0160+
(44)	0.1000	0.0054+	0.0072+
(45)	0.1000	0.0110+	0.0127+
(46)	0.1000	0.0050—	0.0018—
(47)	0.1000	0.0017—	0.0008—

From these results it is plain that it is a far more difficult matter to dehydrate and dissolve calcium chloride than either magnesium chloride or lithium chloride. The separation of the chlorides of sodium and potassium from calcium chloride cannot be accomplished, for the quantities employed in these experiments, by a single precipitation; but the repetition of the treatment is effective. In the residues of experiments (46) and (47) calcium could not be found by the test with ammonium oxalate. In a case, therefore, in which the separation of sodium and potassium from lithium, magnesium, and calcium in one operation should be desirable, the end may probably be accomplished by means of the process here described.

Certain preliminary experiments with the nitrates of the bases under discussion indicate that these are susceptible of similar separation by the action of amyl alcohol; and the wide applicability in analytical operations of the general principle involved, — the dehydrating of salts by means of amyl alcohol or other liquid of high boiling-point and appropriate solvent action, — can scarcely be a matter of doubt.